

PATENT SPECIFICATION

(11) 1336518

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DRAWINGS ATTACHED

- (21) Application No. 32399/72 (22) Filed 11 July 1972
 (31) Convention Application No. 52907 (32) Filed 16 July 1971 in
 (33) Japan (JA)
 (44) Complete Specification published 7 Nov. 1973
 (51) International Classification C09K 1/54
 (52) Index at acceptance
 C4S 311 43Y 714 739 758 771 78Y
 (72) Inventors MINORU WATANABE and TSUNEYO SUMITA



ERRATA

SPECIFICATION No. 1,336,518

Page 1, line 47, after with insert trivalent cerium

Page 1, line 77, for 542 g read 5.42 g

THE PATENT OFFICE
 4th August, 1975

20 should retain an afterglow for a long time and indicate prominent luminescence.
 Any of the conventional phosphor materials has the drawback that where practically applied as a phosphor screen, for example, to a flying spot scanner, it is degraded in quality
 25 by irradiation of electron beams. Therefore there has grown demand for development of a phosphor material capable of emitting intense luminescence.
 The phosphor material of this invention
 30 retains an afterglow only for an extremely short time and has a luminescent region extending from the ultraviolet rays to the shorter wave rays of visible light which matches well with, for example, that of the
 35 S-4 photoelectric surface, thus indicating a high luminescent efficiency. Accordingly, the phosphor material of the invention is adapted for use not only with a flying spot scanner and electronic video recording apparatus, but
 40 also with a fluorescent lamp for special application and X-ray tube.
 The figure is a curve diagram showing the spectrum of luminescence emitted by a phosphor material according to this invention.

emits intense bluish violet luminescence.

This invention will be more fully understood by reference to the examples which follow.

Example 1.

The mole ratio in which lutetium oxide and yttrium oxide were mixed in this Example 1 corresponds to the case where the coefficient x given in the later described table of mole ratios is 0.4.

The following materials were used in the proportions indicated opposite thereto.

| | |
|--|---------|
| Lutetium oxide (Lu_2O_3) | 6.37 g |
| Yttrium oxide (Y_2O_3) | 542 g |
| Silicic anhydride (SiO_2) | 3.60 g |
| Cerous chloride heptahydrate ($\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$) | 0.298 g |

The above materials were fully mixed with addition of distilled water. After dried, the mixture was placed in a silica crucible, and, with a cap on, baked 4 hours at a temperature of 1350C with a small amount of car-

SEE ERRATA SLIP ATTACHED

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(54) PHOSPHOR MATERIAL

(71) We, TOKYO SHIBAURA ELECTRIC COMPANY LIMITED, a Japanese corporate body, of 72 Horikawa-cho, Saiwai-ku, Kawasaki-shi, Japan, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a novel type of phosphor material adapted for use, for example, with a flying spot scanner and electronic video recording apparatus.

Phosphor materials of such type known to date include, for example, cerium activated calcium-magnesium silicate and cerium activated yttrium silicate. Practical requirements for these phosphor materials are that they should retain an afterglow for a very short time and indicate prominent luminescence.

Any of the conventional phosphor materials has the drawback that where practically applied as a phosphor screen, for example, to a flying spot scanner, it is degraded in quality by irradiation of electron beams. Therefore there has grown demand for development of a phosphor material capable of emitting intense luminescence.

The phosphor material of this invention retains an afterglow only for an extremely short time and has a luminescent region extending from the ultraviolet rays to the shorter wave rays of visible light which matches well with, for example, that of the S-4 photoelectric surface, thus indicating a high luminescent efficiency. Accordingly, the phosphor material of the invention is adapted for use not only with a flying spot scanner and electronic video recording apparatus, but also with a fluorescent lamp for special application and X-ray tube.

The figure is a curve diagram showing the spectrum of luminescence emitted by a phosphor material according to this invention.

The phosphor material of this invention is prepared by activating a matrix consisting of silicates of lutetium and yttrium with preferably by first mixing lutetium oxide, silicic anhydride and yttrium oxide as raw materials with compounds of trivalent cerium as an activating agent. The compounds of trivalent cerium include, for example, cerous chloride, cerous hydroxide and cerous nitrate. Then the mixture is baked several hours at a prescribed temperature in a reducing or oxygen-free atmosphere. A phosphor material thus prepared is further baked several hours at said temperature to obtain a desired product.

When excited by electron beams or ultraviolet rays having wave lengths of, for example, 3650 Å and 2537 Å, then a phosphor material formed of cerium activated lutetium-yttrium silicate according to this invention emits intense bluish violet luminescence.

This invention will be more fully understood by reference to the examples which follow.

Example 1.

The mole ratio in which lutetium oxide and yttrium oxide were mixed in this Example 1 corresponds to the case where the coefficient x given in the later described table of mole ratios is 0.4.

The following materials were used in the proportions indicated opposite thereto.

| | | |
|--|---------|----|
| Lutetium oxide (Lu_2O_3) | 6.37 g | |
| Yttrium oxide (Y_2O_3) | 542 g | |
| Silicic anhydride (SiO_2) | 3.60 g | |
| Cerous chloride heptahydrate ($\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$) | 0.298 g | 80 |

The above materials were fully mixed with addition of distilled water. After dried, the mixture was placed in a silica crucible, and, with a cap on, baked 4 hours at a temperature of 1350°C with a small amount of car-

SEE ERRATA SLIP ATTACHED

- bon powders spread on the surface of the mixed mass, and, after quenched, was further baked 3 hours similarly at a temperature of 1350°C. When excited by electron beams (acceleration voltage 10 KV; current density 1 $\mu\text{A}/\text{cm}^2$), then a phosphor material prepared from cerium activated lutetium-yttrium silicate under the above-mentioned conditions emitted intense bluish violet luminescence. It was confirmed that the intensity of said luminescence was 151 percent higher, as shown under the item $x = 0.4$ in Table III given later, than that of the prior art cerium activated calcium-magnesium silicate phosphor (designated as No. P-16 by the Joint Electron Device Engineering Council). Further, the phosphor material of this invention indicated, as seen from Table I below, substantially the same luminescence spectrum as that of the conventional phosphor materials of the similar kind. The characteristics of said spectrum are presented in the appended drawing. Table I below shows the peak values of the luminescence spectrum and the luminescence limit values on the longer wave side of the phosphor materials of the prior art and those of this invention.

TABLE I

Luminescence characteristics when excited by electron beams

| Phosphor material | | Peak values (nm) of luminescence spectrum | Luminescence limit values (nm) on the longer wave side |
|-------------------|-----------------------------------|---|--|
| Cerium activated | Lutetium silicate | 388 | 485 |
| | Lutetium-yttrium silicate | 394 | 520 |
| | Calcium-magnesium silicate (P-16) | 391 | 465 |
| | Yttrium silicate | 395 | 532 |

- The mole ratio in which the raw materials ably mixed is shown in Table II below. of the phosphor of this invention are prefer-

TABLE II

Mole ratio of raw materials

| Raw material | Mole ratio |
|------------------------------|------------|
| Lutetium oxide | 2x |
| Yttrium oxide | 2 (1-x) |
| Silicic anhydride | 3 |
| Cerous chloride heptahydrate | 0.04 |

In Table II above, x denotes a number larger than zero but smaller than 1.

Example 2.

- Samples of a phosphor material were prepared through substantially the same series of steps as in Example 1 by changing the values of the coefficient x shown in the preceding Table II of the mole ratio as to 1, 0.8, 0.6, 0.4, 0.2, 0.1, 0.05 and 0. Where x

denoted 1, the phosphor material was prepared from lutetium oxide alone; and where x represented 0, it was formed of yttrium oxide alone. Accordingly, these phosphor materials were prepared simply as referential samples.

The phosphor samples prepared by chang-

ing the values of the coefficient x as described above were excited by electron beams (acceleration voltage 10KV; current density $1 \mu\text{A}/\text{cm}^2$) as well as by ultraviolet rays (3650 Å). The luminescence intensity of the samples was measured by a S-4 photo cathode for each case of excitation, the results being presented in Tables III and IV below.

TABLE III

Luminescence characteristics when excited by electron beams

| Value of x | Relative luminescence intensity to P-16 phosphor (%) | Peak value of luminescence spectrum (nm) |
|--------------|--|--|
| 1 | 136 | 388 |
| 0.8 | 143 | 392 |
| 0.6 | 146 | 393 |
| 0.4 | 151 | 394 |
| 0.2 | 131 | 394 |
| 0.1 | 128 | 394 |
| 0.05 | 123 | 394 |
| 0 | 87 | 395 |

TABLE IV

Luminescence characteristics when excited by ultraviolet rays

| Value of x | Relative luminescence intensity to P-16 phosphor (%) | Peak value of luminescence spectrum (nm) |
|--------------|--|--|
| 1 | 350 | 388 |
| 0.8 | 457 | 401 |
| 0.6 | 449 | 399 |
| 0.4 | 476 | 401 |
| 0.2 | 435 | 400 |
| 0.1 | 410 | 400 |
| 0.05 | 350 | 400 |
| 0 | 302 | 400 |

As collectively judged from the data given in both Tables III and IV, the phosphor materials of this invention may be well deemed to have better luminescence characteristics than the referential samples of cerium activated lutetium silicate ($x = 1$) and cerium activated yttrium silicate ($x = 0$). Where excited by electron beams, a phosphor material whose raw materials were mixed in the molar ratio in which the coefficient x was

particularly taken to be 0.4 displayed, as seen from Table III, luminescence intensity 151 percent higher than the prior art phosphor material P—16. As apparent from
5 Tables III and IV, the values of the coefficient x (which also correspond to the mole ratio of the final product) are preferred to range between 0.05 and 0.8, that is, the mole
10 ratio of lutetium silicate to yttrium silicate included in the phosphor material of this invention is desired to be larger than 0.05, but smaller than or equal to 4.

WHAT WE CLAIM IS:—

15 1. A phosphor material characterized in that it is prepared by activating a matrix con-

sisting of silicates of lutetium and yttrium with trivalent cerium.

2. A phosphor material according to claim 1 wherein the mole ratio of lutetium silicate to yttrium silicate is larger than 0.05, but
20 smaller than or equal to 4.

3. A phosphor material according to claim 1, substantially as hereinbefore described with reference to the examples.

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